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6. AUTHOR(S)
Dr. Dan D. Edie

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Clemson University
Box 340903; 123 Earle Hall
Chemical Engineering
Clemson, SC 29634-0909

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13. ABSTRACT (Maximum 200 words)

This project proved that, unlike other precursor fibers (rayon, polyacrylonitrile (PAN) and pitch), phenylenebenzobisoxazole (PBO) can be directly converted to carbon fiber without prior stabilization. More importantly, when directly carbonized, the PBO-based carbon fibers developed moduli and thermal properties similar to pitch-based carbon fibers. This ability to develop high moduli and thermal conductivity could make PBO an attractive reinforcing fiber for many carbon/carbon applications. Thus, a process for forming potentially low-cost carbon/carbon composites using PBO fibers was also evaluated. In this process PBO fibers were coated with phenolic and high melting pitches using a novel suspension coating technique, and then directly thermoformed into carbon/carbon composites. No stabilization step was needed, and the fibers and matrices were carbonized simultaneously. The resulting carbon/carbon composites exhibited properties similar to those of many commercial composites.

Thus, the project demonstrated that PBO can be suspension coated with either a phenolic or pitch matrix, formed into a complex preform and directly carbonized to produce a carbon/carbon composite. This process eliminates the lengthy stabilization period and carbonizes both the fiber and the matrix in a single step.

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Final Technical Report
(01 Oct 1994 - 30 Sept 1998)

ONR CONTRACT INFORMATION

Contract Title: HIGH THERMAL CONDUCTIVITY FIBERS FROM PBO

Performing Organization: Clemson University

Principal Investigator: Dan D. Edie
[Ph. (864) 656-3056, FAX (864) 656-0784]

Contract Number: N00014-94-1-1159 (CU REF: 05-5911)

R & T Project Number: ccassrt---01

ONR Scientific Officer: A. K. Vasudevan

A. Research Goals

The first goal of the project is to examine the conversion of poly p-phenylenebenzobisoxazole (PBO) to carbon fiber. Because of PBO's structure, carbonized PBO fibers should exhibit relatively high thermal conductivities. The second goal of the project is to form low-cost, high-thermal-conductivity carbon/carbon composites by combining PBO fiber with highly carbonaceous matrices that can be directly carbonized.

B. Significant Results

Unlike precursor fibers (rayon, polyacrylonitrile (PAN) and pitch), phenylenebenzobisoxazole (PBO) can be directly converted to carbon fiber without prior stabilization. This project showed that these PBO-based carbon fibers developed strengths and moduli similar to pitch-based carbon fibers. In the final stage of this research a technique was developed to form potentially low cost carbon/carbon composites using PBO fibers. PBO fibers were coated with phenolic and high melting pitches using a novel powder coating process, and then directly thermoformed into carbon/carbon composites. No stabilization step was needed, and the fibers and matrices were carbonized simultaneously.

PBO-Based Carbon Fibers

The production of polymer-based carbon fibers usually involves heating the precursor fiber to approximately 300°C in air to crosslink the polymeric structure, rendering it infusible, and then heating the crosslinked fiber to much higher temperatures (from 2000 to 3000°C) to drive off most non-carbon elements. During the first two years of the project, the various stages of this conversion process for PBO precursor fibers were studied. This work developed a provided a fundamental understanding of the PBO-carbon fiber conversion process.

During oxidative stabilization, oxygen creates crosslinks between the polymer chains within the PBO fiber. This oxygen must come from either the precursor and/or the surrounding air. Therefore, fiber mass gain normally is used as a measure of the effectiveness of fiber stabilization in air. To test the oxygen uptake of PBO fibers, 2.5 milligrams of PBO fiber were heated in a TGA pan under air from room temperature to 800°C. As Figure A indicates, no detectable mass gain occurred. This indicates that the oxygen from the air is not retained by the PBO fiber. Thus, stabilization in air would not result in the increased oxygen crosslinking commonly observed in other polymers such as PAN.

A series of three stabilization trials were performed. Each of the three samples was heated at a rate of 5 °C per minute to 310 °C and held at that temperature for 30, 60, and 120 minutes, respectively. Finally, all three stabilized fiber samples were heated to 2000 °C at a rate of 20 °C per minute. A length of as-received PBO fiber also was carbonized and served as a control.

Final results showed that stabilization did not enhance the tensile properties of the final carbon fiber. Neither tensile strength nor modulus improved with stabilization, regardless of the stabilization dwell time. This indicates that the expensive and time-consuming stabilization step may be completely eliminated from the carbonization process without adversely influencing the properties of the fiber.

In Dow's pilot-scale PBO process, the fiber is heat treated to a temperature of 550°C for 10-30 seconds in order to enhance its crystallinity and modulus. However, our research indicated that the balance of properties can be altered substantially by additional heating below 540°C. The fiber was heated under argon to a temperature of 530°C and maintained for fifteen minutes, before the fiber was allowed to cool to room temperature. As Table 1 shows, this additional heat treatment reduced the fiber's tensile strength but increased its modulus. More importantly, the additional low temperature treatment substantially increased the fiber's compressive strength.

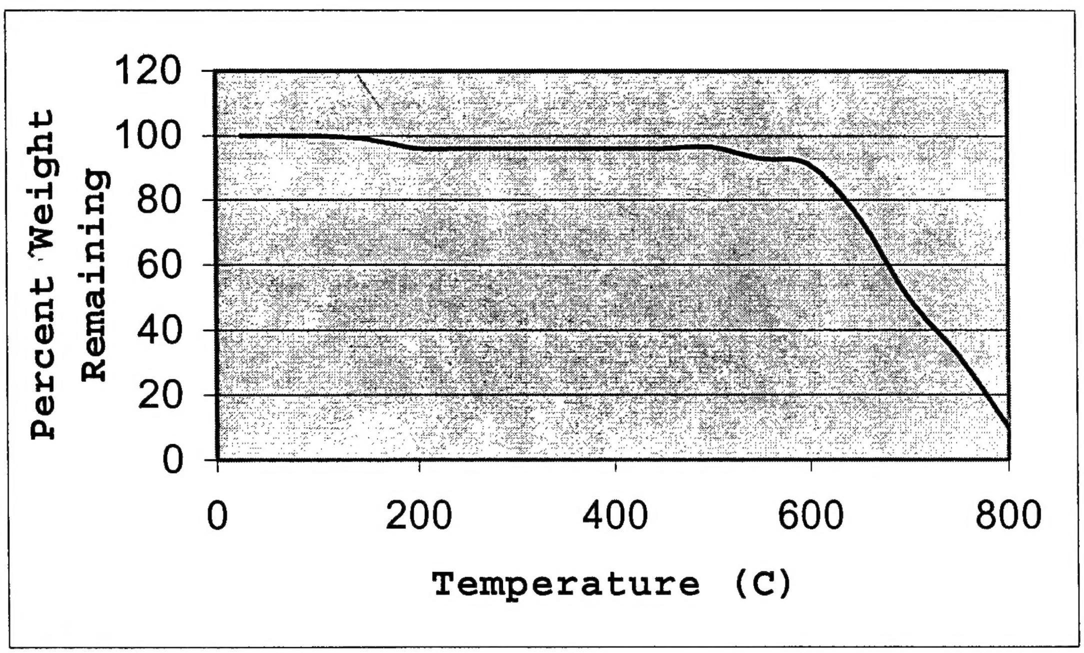

Figure 1: Thermogravimetric analysis profile of PBO fibers in air.

Table 1. Mechanical Properties of PBO Fibers Before and After Heating.

Property	As-Received	Heat Treated
Tensile Strength (MPa)	4130	2700
Tensile Modulus (GPa)	146	211
Compressive Strength (MPa)	380	620

X-ray diffraction analyses of as-received and carbonized fibers proved that the fibers pass from their initially ordered liquid crystalline state to an amorphous form at approximately 600°C. Above 600°C, the disordered carbon remnants begin forming a turbostratic structure, and this turbostratic structure continues to develop throughout the graphitization process.

Then, at temperatures above 1600°C, carbonized PBO fibers begin to develop three-dimensional order. As this order develops, the average interlayer spacing between graphene plane decreases. Fibers with interlayer spacing greater than 3.42 angstroms are considered disordered or turbostratic, while fibers with interlayer spacing less than 3.42 angstroms are considered ordered, or graphitic.

Figure 2 shows that carbonized PBO fibers become increasingly ordered with elevated treatment temperatures. The first signs of long range order appear at 1600°C, where the average interlayer spacing is nearly 3.45 angstroms. The fiber develops more order as temperatures rise, finally becoming "graphitic" at 2400°C.

Crystalline graphite has a mean interlayer spacing of 3.35 angstroms. Thus, even though the carbonized PBO fiber still does not approach the crystallinity of graphite, it is significantly more graphitic than carbon fibers produced from other polymeric precursors such as PAN.

Electrical resistivity tests were performed on the carbonized PBO fibers. Ideally, the electrical resistivity should decrease when the fiber is treated at higher temperatures because of the increased molecular ordering associated with elevated treatment temperatures. However, Figure 3 shows that the electrical resistivity of PBO-based carbon fiber decreased with increasing temperature only to 1400 °C. Above this temperature an increase in electrical resistivity is observed.

The electrical resistivity of PBO-based carbon fibers produced in a continuous operation at 2200°C was found to be approximately 9 $\mu\Omega$-m. This value compares favorably with essentially all carbon fibers produced from

polymer precursors. Additionally, the resistivity places PBO in the conductivity range of some commercial mesophase pitch-based carbon fibers.

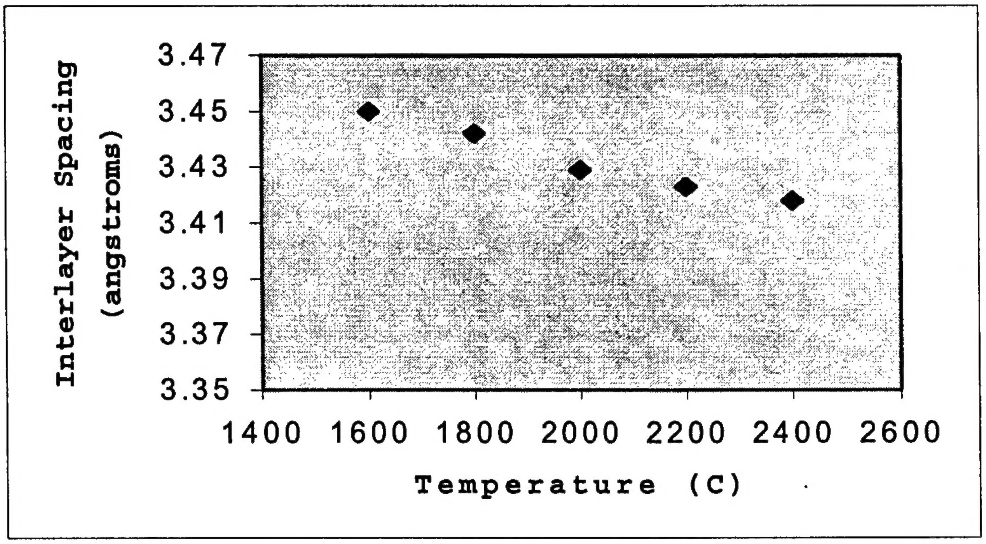

Figure 2: The influence of treatment temperature on interplanar spacing.

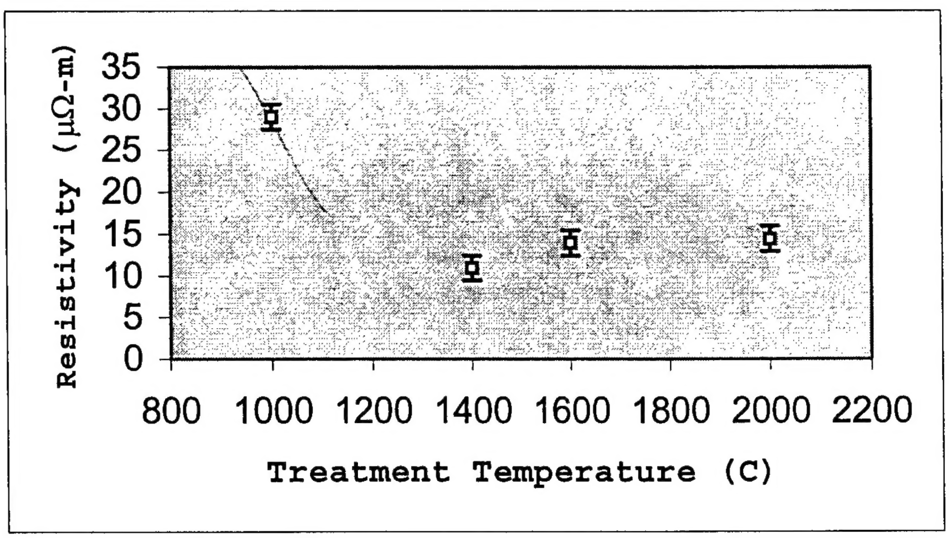

Figure 3: The influence of temperature on the electrical resistivity of PBO-based carbon fibers.

PBO-Based Carbon/Carbon Composites

In the third year of the research, PBO fibers were combined with carbonaceous matrix precursors and formed into carbon/carbon (CC) composites using a single carbonization step. Three different matrix materials were

evaluated: a phenolic resin, an alumina-loaded phenolic resin, and a coal tar pitch. In the first series of tests, PBO fibers were coated with the phenolic resin using a powder coating method and a suspension coating method. Then, the coated fibers, or towpreg, were wrapped on a fiber mandrel, forming unidirectional specimens. Finally, the unidirectional specimens were placed in a heated press and consolidated at 1100°C into unidirectional CC composites. The objective of this series of tests was twofold: (i) determine the void content and crack pattern for this fiber/matrix combination and (ii) determine which of the two coating methods produces the more consistent CC composite.

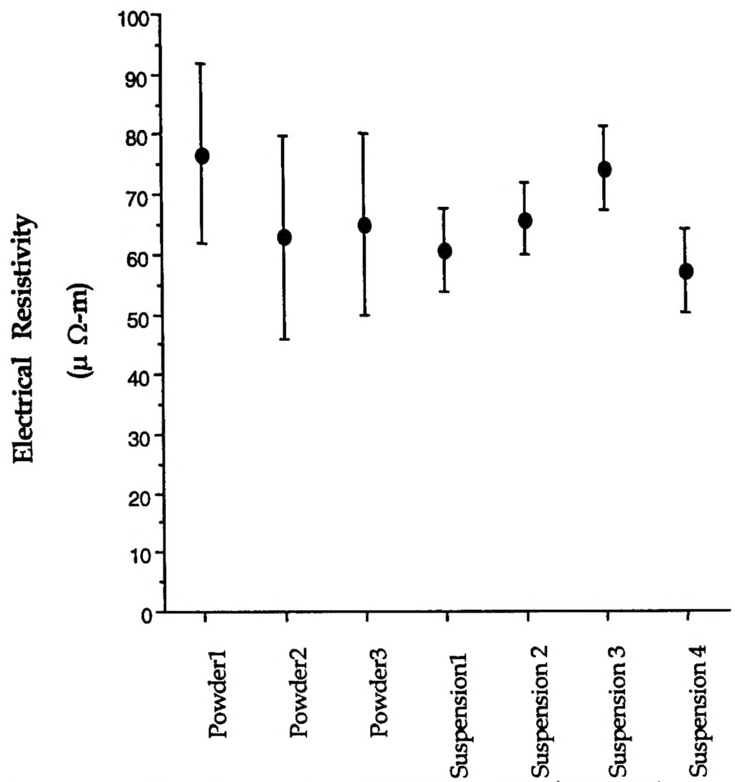

Figure 4: Comparison of carbonized PBO/phenolic carbon/carbon composites by coating method

Several of the CC composites formed using each of the coating methods were cross-sectioned, mounted and polished to determine the degree of interfacial bonding. Optical inspection of all samples revealed few cracks or voids at fiber/matrix interfaces, indicative of strong fiber-matrix bonding. This may have been the result of simultaneous shrinkage during carbonization or interaction between the PBO fiber and the phenolic resin prior to, or during carbonization. As expected, numerous small voids and cracks, created the evolution of gases during composite carbonization, could be observed throughout the matrix. However, because of the strong

interfacial bonding, the samples also developed cracks perpendicular to the fiber direction to relieve accumulated stresses created during carbonization.

The average electrical resistivity as well as the range of measured values for thirty CC composite specimens prepared by these two coating techniques (using the same nominal process conditions) are shown in Figure 4. As the figure shows, the suspension coating method produced CC composites with more consistent electrical resistivities. Because of this, the suspension coating method was used in all subsequent experiments. It should be noted these electrical resistivities, measured parallel the fiber axis, were greater than expected. These high resistivities apparently were caused by the stress cracks perpendicular to the fiber axis. Such a crack pattern inhibits the flow of current, and thus, the flow of heat. Obviously, this type of cracking must be minimized if the thermal properties of the CC are to be maximized.

To address this issue, a second series of CC samples were prepared and tested. These samples were prepared by evenly mixing 10 μm in diameter alumina powder particles throughout the phenolic resin, applying this mixed matrix to the PBO fiber using the suspension coating technique, and then thermoforming the coated tows into unidirectional CC composites. The alumina powder was added to create additional interfaces (alumina-phenolic) which could relieve residual stresses during carbonization. The objective was to decrease the size of the matrix cracks. Surprisingly, this alternate stress-release mechanism appeared to reduce not only the size of the cracks, but also the amount of matrix cracking. These smaller stress cracks caused a decrease of the resistivity of the carbonized composites (see Figure 5).

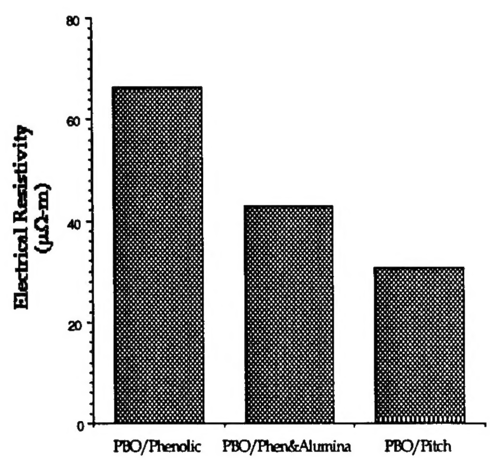

Figure 5: Comparison of carbonized composites containing PBO fibers with different matrices

In a third series, PBO fibers were coated with a coal tar pitch using the suspension coating method and thermoformed into CC composites. Here the objective was to use a highly carbonaceous matrix precursor to decrease void formation during carbonization and, possibly, reduce the amount of interfacial bonding by using a matrix material which is less likely to interact with PBO during carbonization. Again the CC specimens were mounted, cross-sectioned, polished, and inspected to determine the degree of interfacial bonding. Optical inspection revealed that this fiber/matrix combination resulted in enough interfacial cracking to effectively eliminate the stress cracks perpendicular to the fiber axes. Because of this, as Figure 5 shows, the coal tar-based CC composites exhibited lower resistivities than either the phenolic-based or the alumina/phenolic-based carbon/carbon composites.

D. List of Publications/Reports/Presentations

1. Papers Published in Refereed Journals

"Direct Carbonization of PBO Fiber," J. A. Newell, D. K. Rogers, D. D. Edie, and C. C. Fain, *Carbon*, **32** (4), pp. 651-658 (1994).

"Factors Limiting the Tensile Strength of PBO-Based Carbon Fiber," J. A. Newell and D. D. Edie, *Carbon*, **32** (4), pp. 651-658 (1994).

"Kinetics of Carbonization and Graphitization of PBO Fiber," J. A. Newell, D. D. Edie and E. Loren Fuller, *Journal of Applied Polymer Science*, 60, pp. 825-832 (1996).

"The Effect of Processing on the Structure and Properties of Carbon Fibers," D. D. Edie, *Carbon*, **36** (4), pp. 345-362 (1998).

Steady and Transient Rheological Behavior of Mesophase Pitches," O. Fleurot and D. D. Edie, Journal of Rheology, 42 (4), pp. 781-793 (1998).

"Ribbon Fibers from Naphthalene-Based Mesophase: Surface Studies and Fiber/Matrix Interactions in Polycarbonate Composites," M.C. Paiva, M. Nardin, D. D. Edie, and C.A. Bernardo, *Carbon*, **36**, (1-2), pp. 71-78 (1998).

2. Non-Refereed Publications and Published Technical Reports

"High Thermal Conductivity Carbon/Carbon Composites Made from PBO-Based Carbon Fibers," C. D. Mundt, and D. D. Edie, Carbon 97, Proceedings of the 23rd Biennial Conference on Carbon, State College, PA, July 18-23, Vol. II, pp. 540-541 (1997).

"Viscoelastic Behavior of Air-Blown Pitches," O. Fleurot, R. Menendez, C. Blanco, R. Santamaria, J. Bermejo, and D. D. Edie, Carbon 97, Proceedings of the 23rd Biennial Conference on Carbon, State College, PA, July 18-23, Vol. II, pp. 190-191 (1997).

"The Influence of Thermal Treatment on the Rheology of Coal Tar Pitches," R. Menendez, J. Bermejo, O. Fleurot, and D. D. Edie, Carbon 97, Proceedings of the 23rd Biennial Conference on Carbon, State College, PA, July 18-23, Vol. II, pp. 204-205 (1997).

"High thermal Conductivity Carbon/Carbon Composites Made from a Novel Process," C. M. Mundt and D. D. Edie, **Carbon '96**, Proceedings of the 7th International Conference on Carbon, New Castle-upon-Tyne, England, July 7-12, pp. 709 (1996).

3. Presentations

a. Invited

"The Effect of Processing on the Structure and Properties of Carbon Fibers," D. D. Edie, CASS/CCMS Sixth Technical Conference, Virginia Polytechnic Institute and State University, Blacksburg, VA, April 19-21, 1998.

"Preparation and Structure of High Thermal Conductivity Carbon Materials," D. D. Edie, Gordon Research Conference on Hydrocarbon Resources, Ventura, California, January 12-17, 1997.

"The Effect of Processing on the Structure and Properties of Carbon fibers," D. D. Edie, NATO Advanced Study Institute, Design and Control of Structure of Advanced Carbon Materials for Enhanced Performance, Antalya, Turkey, May 10-20, 1998.

b. Contributed

"Factors limiting the Tensile Strength of PBO-Based Carbon Fibers," J. A. Newell and D. D. Edie, <u>1994 Annual AIChE Meeting</u>, San Francisco, CA, November 13-18, 1994.

"Transient and Steady shear Behavior of Carbonaceous Mesophase," O. Fleurot and D. D. Edie, <u>1996 Annual AIChE Meeting</u>, Chicago, IL, November 10-15, 1996.

4. Books (and sections thereof)

"Spinning of Carbon Fiber Precursors," D. D. Edie, J. J. McHugh, and J. A. Newell, in The Science of Carbon Materials, Harry Marsh, ed., Elsevier Science, Ltd., in press.

E. <u>List of Honors/Awards</u>

Name of Person Receiving Award	Recipient's Institution	Name, Sponsor, and Purpose of Award
Dan Edie	Clemson University	Elected President of the American Carbon Society
Dan Edie	Clemson University	Plenary Lecture at 23rd Biennial Conference on Carbon

F. <u>Participants</u>

James A. Newell, completed Ph. D. in Chemical Engineering and graduated from Clemson University in December, 1994.

Chad Mundt, Ph. D. student in Chemical Engineering and currently enrolled at Clemson University.

Jeff Meece, M. S. student in Chemical Engineering and currently enrolled at Clemson University.

All of the above are U. S. citizens.

G. <u>Other Sponsored Research During Grant Period</u>

<u>This Grant</u>

"High Conductivity Fibers From PBO," Sponsored by ONR, 0% of time, $30, 392/yr, 7/31/94 to 8/1/98.

Other Grants

"High Thermal Conductivity Ribbon-Shaped Fibers," Sponsored by ONR, 30% of time, $566,658/yr, 12/31/95 to 4/30/99.

"Supercritical Fluid Extraction for High Thermal Conductivity Fibers, Sponsored by DEPSCoR, 15% of time, $100,000/yr, 9/1/94 to 8/31/98

"Center for Advanced Engineering Fibers and Films - Engineering Research Center," Sponsored by NSF, 40% of time, $300,000/yr, 8/1/98 to 7/31/03

"Carbon Fibers and C/C Composites from Supercritically Extracted Precursors," Sponsored by DEPSCoR, 10% of time, $60,000/yr, 12/30/97 to 12/31/00

"Fiber-Matrix Bonding and Physical Properties of C/C Composites," Sponsored by NSF, 0% of time, $11,055, 9/1/96 to 8/31/99.

"High Thermal Conductivity Fibers," Sponsored by Great Lakes Composite Consortium, $220,000/yr, 30% of time, 1/1/92 to 12/31/95.

"High Thermal Conductivity Carbon/Carbon Composites, Office of Naval Research," $31,100/yr, 0% of time, 10/1/92 to 9/31/95.

"Production of Carbon Monofilament - Phase II," sponsored by MSNW, $150,000/yr, 5% of time, 3/3/95 to 5/3/96.

"Engineering Fibers and the Micromechanics of Their Composites," Sponsored by NSF, $95,000/yr, 17% of time, 7/1/92 to 6/31/95.

H. Summary for Grant Period
Publications/Patents/Presentations/Honors/Participants
(Number Only)

	ONR	Non-ONR
a. Number of Papers Submitted to Refereed Journal but not yet published:	0	4
b. Number of Papers Published in Refereed Journals:	6	8
c. Number of Books or Chapters Submitted but not yet Published:	1	0
d. Number of Books or Chapters Published:	0	0
e. Number of Printed Technical Reports & Non-Refereed Papers:	4	16
f. Number of Patents Filed:	0	0
g. Number of Patents Granted:	0	0
h. Number of Invited Presentations at Workshops or Professional Society Meetings:	3	3
i. Number of Contributed Presentations at Workshops or Professional Society Meetings:	2	5
j. Honors/Awards/Prizes for Contract/Grant Employees: (selected list attached)	2	2
k. Number of Graduate Students and Post-Docs Supported at least 25% on contracted grant:	3	12
Grad Students: TOTAL	3	11
Female	0	2
Minority	0	0
Post Doc: TOTAL	0	1
Female	0	1
Minority	0	0
l. Number of Female or Minority PIs or CO-PIs:		
New Female	0	0
Continuing Female	0	1
New Minority	0	0
Continuing Minority	0	0